PATENT SPECIFICATION

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C3R 22C 3C 3N1 7C 7N7 C10 C11 C12 C13M C13P C13S C1 C21 C22 C23 C24 C28X C29 C32 C33A C33X C4 C5B1 C6A1 C6AX C6B C6X C8B C8P C8R C8T C9A C9B C9N L1B L2C1 L3A L3B L4A L4C L4D L6F
C3B 1C10 1C11 1C12 1C13M 1C13P 1C13S 1C1 1C21 1C22 1C23 1C24 1C28X 1C29 1C32 1C33A 1C33X 1C4 1C5B1 1C6A1 1C6AX 1C6B 1C6X 1C8B 1C8P 1C8R 1C8T 1C9A 1C9B 1C9N 1D2C 1D6 1L1B 1L2C1 1L3A 1L3B 1L4A 1L4C 1L4D 1L6F
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(54) PREPARATION OF LUBRICANT-CONTAINING SYNTHETIC RESIN COMPOSITIONS

(71) We, SUMITOMO ELECTRIC INDUSTRIES, LTD., a Japanese Company, of No. 15, Kitahama 5-Chome, Higashi-Ku, Osaka-Shi, Osaka, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a lubricant-containing polymeric synthetic resin composition and a process for preparing it.

Resins such as polyamides, polyacetals, polycarbonates and polymers of tetrafluoroethylene have been used as wear resistant or low-friction materials. Such materials are fully serviceable under low loads and at low velocities even in the absence of lubricant, but at higher loads and velocities, the frictional heat generated tends to cause softening and charring so that the materials become useless.

Polytetrafluoroethylene has a very low coefficient of friction, but it has poor abrasion resistance. Its abrasion resistance may be improved by a filler such as glass fibres, asbestos, mica, graphite, lead or lead oxide. Unfortunately however, such a filled polytetrafluoroethylene is very expensive.

Polyamides, polyacetals or polycarbonates are cheaper, and their abrasion resistances may be improved by addition of a solid lubricating agent, such as graphite, molybdenum sulphide or a polytetrafluoroethylene powder, but the improvement in abrasion resistance under high loads and at high velocities is only slight.

Other low friction materials are made by sintering synthetic resin and metal powders to form e.g. a bearing, and impregnating with a lubricant. However, synthetic resin powders are expensive, moulding is difficult and the moulded articles produced have very poor strength.

On the other hand, it is well known that when an external lubricant is supplied, the coefficient of friction of the plastics material may be reduced by at least nine-tenths and its abrasion resistance markedly increased. However, the use of an external lubricant requires a lubricating mechanism, which increases the cost.

An object of this invention is to improve the lubricity and abrasion-resistance of a polymeric synthetic resin composition at low cost and to produce such a composition with good mouldability.

We have disclosed in United States Patent No. 3,779,918, a lubricant-containing plastics composition which is obtained by mixing a lubricant with a lubricant-absorbent carrier having a specific surface area of at least 0.01 m^2/g, and mixing the resulting mixture with a base plastics material (synthetic resin).

We have now found that a lubricant may be incorporated into a base synthetic resin without separation, by (a) mixing a lubricant with at least one carrier; and (b) simultaneously or subsequently mixing the resulting mixture with a synthetic resin; wherein the carrier is an organic or inorganic powder having (i) a melting point higher than the moulding temperature of the synthetic resin, (ii) a specific surface area of at least 0.3 m^2/g and (iii) an oil absorbance as defined herein of at least 0.2 cc of oil per cc of carrier; and the amount of lubricant used is 2 to 40% of the volume of the composition, and not more than 10.00 times the total oil absorbance of the carrier.

The organic or inorganic powder carrier

should be as fine as possible, and have a specific surface area of at least 0.3 m^2/g, desirably at least 0.9 m^2/g, and preferably at least 3 m^2/g. Powders having a surface area of less than 0.3 m^2/g have the defects that large particles are dispersed in the base plastics such that the surface condition of the moulded articles, and the critical oil absorbtion is low so that a larger quantity of the carrier is necessary which in turn causes a reduction in strength.

The term " oil absorbance " as used herein is defined as the ratio of the volume of lubricant absorbed to the volume of the carrier, as measured at 20° C when the melting point of the lubricant is not more than 0° C, and at the melting point plus 20° C when the melting point of the lubricant exceeds 0° C. This value should be as large as possible—at least 0.2 cc/cc, desirably at least 0.6 cc/cc. If the value is less than 0.2 cc/cc, the lubricant tends to be separated, and the amount of the carrier is large as compared with the lubricant, resulting in a deterioration of the thermal stability of the composition.

The amount of the lubricant to be incorporated is not more than 10.0 times the total oil absorbance of the carrier, preferably not more than 5.0 times its oil absorbance; when more than 10.0 times the total oil absorbance is used, the lubricant tends to separate during moulding.

The amount of lubricant is 2 to 40% by volume, desirably 5 to 25% by volume of the entire composition. If it is less than 2%, the abrasion resistance of the composition is little improved, while if it is above 40%, the strength and abrasion resistance are reduced.

The lubricant is optionally a combination of a lubricant oil with an oiliness-increasing agent and at least one of a fire retardant, an antistatic agent and an antioxidant.

According to the invention, it is possible to mix a synthetic resin, a carrier and a lubricant simultaneously in a mixer provided with rotating blades. The composition formed by the process according to the invention is preferably subsequently moulded at the moulding temperature of the resin.

When the base resin (such as a polyacetal) is melted and mixed with a lubricant (such as a paraffin oil) and a carrier in a monoaxial screw extruder, it is difficult to disperse the lubricant sufficiently in the resin. Since the polymer is not compatible with the lubricant, after the polymer has been swollen with the lubricant, the remainder of the lubricant is adsorbed to the surface of the carrier or absorbed therein. However, a part of the lubricant separates from the interior of the polymer, and thus separates from the molten polymer and the carrier, after which the lubricant may begin to decompose. The separated lubricant may adhere to the screw and the cylinder wall of the extruder, thus causing difficulties in extrusion.

It is desirable to prepare a water-in-oil type emulsion (hereinafter referred to as a w/o type emulsion) by mixing and dispersing such incompatible substances as a resin and a lubricant, since even wholly incompatible substances may be intimately mixed in this way. We have found that if a molten polymer and a lubricant oil are stirred together using a low-shear kneader having a great stirring effect a stable w/o type emulsion is performed, little lubricant separates and adheres to the mixing equipment. Suitable low shear kneaders are multi-axial extruders (having at least two axes) or an optionally heated mixing machine having two or more rotors, such as a Banbury mixer or calender rolls.

The accompanying drawing shows diagrammatically in end view various suitable types of multi-axial rotor. Figs. 1 and 2 show biaxial rotors and Figs. 3 and 4 show triaxial rotors. Figs. 1 and 3 show rotation in different directions, Figs. 2 and 4 in the same direction. Preferred are closed kneaders, by means of which oxidation of the molten polymer and the lubricant by air are minimised.

In order to obtain water-in-oil emulsions, the use of kneaders having two intermeshing rotors are preferred, in which two rotors (or screws) rotate in different directions (see Figs. 1 and 3) because such a kneader exhibits a reduced shearing action and ensures good stirring effects, thus enabling more lubricant to be included stably. The speed of rotation of the kneader is preferably at least 7 rpm, especially at least 20 rpm. If it is less than 7 rpm, separation of the lubricant may occur. In the most preferred embodiment it is possible to include 2 to 40% by volume of lubricant by the use of a multiaxial screw-type extruder with counter-rotating screws. Such an extruder is preferably continuous and is vented. Desirably, the ratio of the length (L) to the diameter (D) of the screw (L/D) is at least 20, preferably at least 25.

The master batch method may also be used in this invention, whereby pellets of a high lubricant-content are produced by the method described above, and dry blended in any desired proportions with resin not containing the lubricant. By this method, the base resin is subjected to less heating so that a deterioration in properties is minimised.

Examples of the synthetic resins used in this invention include polyethylene, polypropylene, acrylonitrile/butadiene/styrene copolymers, polycarbonates, polyacetals, polyamides, polyphenylene oxide, poly(butylene terephthalate), poly(ethylene terephthalate), poly(phenylene sulphide) and polystyrene.

The following are examples of the powdered carrier.

1. Organic Synthetic resins (List 1)

Polyamides, poly(tetrafluoroethylene), poly-

carbonates, phenolic resins, epoxy resins or diallyl phthalate resins.

2. Inorganic substances (List 2)
   (1) Carbon such as carbon black, graphite or activated carbon.
   (2) Minerals comprising as major components calcium carbonate, basic magnesium carbonate, clay, talc, silica, silicates, mica, quartz, diatomaceous earth, asbestos, aluminium hydroxide, alumina or acid clay.
   (3) Metal oxides such as lead oxide, titanium oxide, or copper oxide.
   (4) Metal nitrides such as titanium nitride or boron nitride.
   (5) Metals such as iron, copper or aluminium.
   (6) Sulphides such as MoS_2.

The carrier used in this invention is believed to act as a surface active agent when a water-in-oil emulsion is prepared and stabilized.

The lubricant may be selected from a wide range of mineral oils such as spindle oil, refrigerator oil, dynamo oil, turbine oil, machine oil, cylinder oil or gear oil, greases, synthetic oils such as hydrocarbons, esters, polyglycols, polyphenyl ethers, silicone oils, and halocarbon-type synthetic oils.

Suitable oiliness-increasing agents are a saturated or unsaturated fatty acid, a fatty acid ester, and aliphatic amide, a metal soap, and/or a higher alcohol. Examples of the oiliness-increasing agent are as follows:

(1) Saturated fatty acids:
capric acid, undecanoic acid, lauric acid, myristic acid, palmatic acid, stearic acid, arachic acid, behenic acid, lignoceric acid, cerotic acid, montanic acid or melissic acid.

(2) Unsaturated fatty acids:
linderic acid, tsuzuic acid, physeteric acid, myristoleic acid, 9-palmitoleic acid, petroselinic acid, oleic acid, elaidic acid, gadoleic acid, gondoic acid, whale oil acid, erucic acid, brassidic acid, selacholeic acid, tallilic acid, xymenic acid, linoleic acid and linveraisic acid.

(3) Fatty acid esters:
Esters of methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, decyl, cocyl, contyl, or oleyl alcohol, and a saturated fatty acid such as acetic acid, caproic acid, enantoic acid, caprylic acid, pelargonic acid, undecanoic acid, lauric acid, myristic acid, palmitic acid, stearic acid, lignoceric acid, cerotic acid, montanic acid or merysic acid, or unsaturated fatty acid such as petroceric acid, an oleic acid, eraidic acid, linoleic acid, linolenic acid, arachydic acid, prasidic acid, ercaic acid, or lisinoleic acid, as well as dibasic fatty acid ester and glycidyl esters.

(4) Fatty acid amides:
octanoylamide, decanoylamide, lauroylamide, myristoylamide, palmitoylamide, stearoylamide, eicosoylamide and docosoylamide.

(5) Metal soaps:
Soaps formed between acids such as stearic acid, oleic acid, palmitic acid or lauric acid and metals such as Li, Be, Mg, Ca, Sr, Cu, Zn, Cd, Al, Ce, Ti, Zr, Pb, Cr, Mn, Co, Ni, Fe, Hg, Ag, Tl or Sn.

(6) Higher alcohols:
octyl, lauryl, cetyl, stearyl or oleyl alcohol.

Suitable fire retardants are at least one compound which may be liquid or powder at the moulding temperature of the synthetic resin, for example one or more of:

1. Phosphoric acid esters

(of formula $O{=}P{-}(OR)_3$):

tris-dichloropropyl phosphate, tris-2-chloroethyl phosphate, tributoxy ethyl phosphate, trimethyl phosphate, triethyl phosphate, tributyl phosphate, trioctyl phosphate, trischloroethyl phosphate, triphenyl phosphate, tricresyl phosphate, trixylenyl phosphate, cresyl diphenyl phosphate, diphenyl mono-*o*-xylenyl phosphate, octylphenyl phosphate, phenyldichloropropyl phosphate, phenyl dichloroethyl phosphate, octyl dichloroethyl phosphate or octyl dichloropropyl phosphate.

2. Halogenated aliphatic hydrocarbons:
dibromotetrachloroethane, tetrabromoethane, 1,2,3,4 - tetrabromobutane, or chlorinated paraffin.

3. Halogenated aromatic hydrocarbons:
chlorinated or brominated aromatics, such as hexabromobenzene or pentabromobenzene.

4. Halogenated alicyclic hydrocarbons:
hexabromocyclododecane.

5. Organotin compounds:

6. Reactive-type fire retardants:
tetrachlorophthalic' anhydride, tetrabromophthalic anhydride, tetrabromo *bis*-phenyl A, *bis*-β-chloroethyl vinyl phosphate, tribromophenyl allyl ether, tribromophenol, tribromoaniline and dibromopropanol.

7. Inorganic compounds:
aluminium hydroxide, sodium borate, antimony oxide, talc, and sodium bicarbonate. (These inorganic compounds are desirably used in intimate admixtures with the compounds 1 to 6 mentioned above).

Suitable antioxidants are at least one of

1. Phenolic compounds:
   1,1 - *bis* - (4 - hydroxyphenyl) - cyclohexanestyrenated phenol,
   2,6-*di-tert.*-butyl-4-methylphenol,
   4,4'-thio*bis*-(6-*tert.*-butyl-3-methylphenol),
   2,2' - methylene - *bis* - (6 - *tert.* - butyl - 4-methylphenol),
   4,4' - butylidene - *bis* - (6 - *tert.* - butyl - 3-methylphenol),
   α- or β-naphthol,

dibutyl-p-cresol,
methylene-*di*-naphthol,
4-isooctylphenol,
3-methyl-2,6-*di-tert.*-butyl-phenol,
2-methylphenol,
4-t-butylphenol,
2,6-dimethylphenol,
4-t-butyl-2-methylphenol,
4-t-octyl-2-methylphenol,
2,4-*di-sec.*-amylphenol,
2,4-di-t-amylphenyl,
2,4-dimethyl-6-t-butylphenol,
2,6-di-t-butyl-4-methylphenol,
2,4,6-tri-t-butylphenol,
4,6-di-t-butyl-2-methylphenol,
4-t-butyl-pyrocatechol,
2,5-di-t-butylhydroquinone,
2,4,5-trihydroxybutyrophenone,
2,2′ - dihydroxy - 4,4′ - dimethoxybenzophenone,
2-hydroxy-4-methoxy-benzophenone,
2,2′-dihydroxy-4-methoxy-benzophenone,
2,4-dihydroxy-4-octoxy-benzophenone,
2,4-dihydroxy-benzophenone.

2. Amines:
N,N′-*di-sec.*-butyl-p-phenylenediamine,
tetramethyl-diaminodiphenylmethane,
phenyl-α-naphthylamine,
phenyl-β-naphthylamine,
1,3-diphenyl-2-propyl-tetrahydroxyamine,
N,N′-*di*-β-naphthyl-p-phenylenediamine,
N,N′-diphenyl-p-phenylenediamine,
N,N′-diallyl-p-phenylenediamine,
N-phenyl-N-isopropyl-p-phenylenediamine,
a polymer of 2,2,4-trimethyl-1,2-dihydroquinoline,
6 - ethoxy - 2,2,4 - trimethyl - 1,2 - dihydroquinoline,
N-phenyl-1-naphthylamine,
N-phenyl-2-naphthylamine,
N - 1 - propyl - N′ - phenyl - p - phenylenediamine, and
N - 1 - phenyl - N′ - cyclohexyl - p-phenylenediamine.

3. Sulphur compounds such as
4-t-butyl thiocresol,
dilauryl-3,3′-thiodipropionate,
4,4′-thiobis-(6-t-butyl-2-methylphenol),
dilauryl thiopropionate,
2-mercaptobenzimidazole, and
distearyl-3,3′-thiodipropionate.

4. Organophosphorus compounds:
triphenyl phosphite,
tris-nonylphenyl phosphite,
alkylaryl phosphites, and
tri-n-butyl phosphite.

The antioxidant may be used in conjunction with an antioxidant promotor such as thiourea, its derivatives, thioacids, thioamides, mercaptopyridine or pyrimidine derivatives.

Suitable antistatic agents are at least one compound as follows:—

1. Anionic compounds:
salts of carboxylic acids, sulphonic acids, higher alcohol sulphate esters, aliphatic sulphonic acids and phosphoric acid esters.

2. Cationic compounds:
salts of primary, secondary, tertiary or quaternary amines, for example, stearamido propyl dimethyl-(β-hydroxyethyl) ammonium nitrate.

3. Amphoteric compounds:
amino acids, carboxylic acids, sulphate ester salts.

4. Nonionic compounds:
polyalkylene ether adducts of carboxylic acids, alcohols or phenol of the alkyl ether type, alkyl ester type or polyethylene imine type, polyalkylene ether adducts of polyamides, or amides.

5. Inorganic compounds:
carbon black, CaF_2, $CaCO_3$, or metal fibres, e.g. of stainless steel or copper with a diameter of several microns to several tens of microns.

The base synthetic resin used in this invention may contain glass fibres, carbon fibres, or metal fibres incorporated in advance or at blending or extruding.

The resin composition of the invention may be used to produce moving parts, for example, light electrical appliance parts such as bearings, cams, gears or rollers, which have a low-friction surface. These devices may be produced by injection moulding or extrusion moulding.

The present invention will now be illustrated by the following Examples, in all of which mixing is by a Henshell type mixer.

The properties of all moulded articles formed in Examples 1 to 11 and Comparative Examples 1 to 6 are given in Table 1, wherein:

* The "*PV value of bearing*" is defined by pressure x velocity ($Kg/cm^2 \times m/min$) which shows the limit at which burning does not occur when a bearing having an inside diameter of 10 mm, an outside diameter of 14 mm and a length of 10 mm is rotated at varying peripheral speeds and under varying loads without the supply of lubricant.

** The *abrasion resistance* is defined by the amount of wear caused to a test piece without the supply of lubricant at a speed of 3.62 m/sec and under a load of 19.8 Kg using an iron disc having an outside diameter of 30 mm and a thickness of 3 mm.

Where the word "burned" appears in the Table, this indicates that the sample underwent melt flow and charring, so that the measurement of the amount of wear becomes impossible.

In other subsequent Tables (Tables 2—6) these terms have the same meaning.

The properties of moulded articles formed by Examples 12 and 13 and Comparative Examples 7 and 8 are shown in Table 2; and by Comparative Examples 9, 10 and 11 in Table 3. The properties of mouldings formed from embodiments containing antioxidants

(Examples 14 to 17), fire retardants (Examples 18 to 20) and antistatic agents (Example 21) are shown in Tables 4, 5 and 6 respectively.

EXAMPLE 1.

3.5% by volume of activated carbon (having a specific surface area of 1015 m^2/g and an oil absorbance of 5.7 cc/cc), 7% by volume of a paraffinic lubricant oil (Ro 2500, a product of Maruzen Oil Co., Ltd.), and 89.5% by volume of polybutylene terephthalate (PBT) (G1030), a product of Toyo Spinning Co., Ltd.) containing 30% by weight of glass fibres were simultaneously mixed in a mixer including rotating blades, and a mixture was moulded using a 32 mm-diameter monoaxial screw type injection moulding machine.

For comparison, G 1030 alone was moulded in the same manner as above (Comparative Example 1).

As shown in Table 1, the tensile strength of the moulded article was somewhat lower according to the invention than in the Comparative Example, but the bearing performance and the abrasion resistance of the moulded article increased markedly.

EXAMPLE 2.

The materials as described in Example 1 were kneaded using a biaxial screw with a screw diameter of 30 mm and an L/D ratio of 28 and adapted to be rotated in different directions. The screw was operated at a speed of 60 rpm, and the temperature of the part below the hopper was maintained at 150° C and that of the cylinder portion at 200° C. The mixture was extruded into an article having a diameter of 3 mm, and then cooled with water. The mixture obtained was cut by a pelletizer to form pellets. At this time, there was no separation of the lubricant. The pellets were moulded by a screw-type injection moulding machine.

As shown in Table 1, the properties of the moulded article were further improved over those of the moulded article obtained in Example 1.

EXAMPLES 3, 4 and 5.

Example 2 was repeated except that (i) 7% by volume of stearic acid (ii) 4% by volume of Ro 2500 and 3% by volume of stearic acid and (iii) 7% by volume of stearyl alcohol, respectively, were used instead of Ro 2500.

EXAMPLE 6.

Example 2 was repeated except that nylon 66 (CM 3001N, a product of Toray Industries, Inc.) was used instead of the polybutylene terephthalate and the amount of the activated carbon was changed to 2.33% by volume.

For comparison, CM3001N alone was moulded in the same way as in Example 2 (Comparative Example 2).

The results as shown in Table 1, show that the abrasion resistance of the moulded article according to the invention was markedly increased.

EXAMPLE 7.

Example 2 was repeated except that nylon 6 (CM 1001 g, a product of Toray Industries, Inc.) containing 30% by weight of glass fibres was used instead of the polybutylene terephthalate, 5% by volume of calcium carbonate having a specific surface area of 31 m^2/g and an oil absorbance of 2.14 cc/cc was used instead of the activated carbon, and the amount of the lubricant Ro 2500 was changed to 10% by volume. As Comparative Example 3, CM 1001 G alone was moulded in the same way.

EXAMPLE 8.

Example 2 was repeated except that a polycarbonate (S—2000, a product of Mitsubishi-Edogawa Chemical Co., Ltd.) was used instead of the polybutylene terephthalate, 2% by volume of MoS_2 having a specific surface area of 8 m^2/g and an oil absorbance of 1.3 cc/cc was used as a carrier, and the amount of the lubricant Ro 2500 was changed to 5% by volume. As Comparative Example 4, S—2000 alone was moulded in the same way as above.

EXAMPLE 9.

Example 2 was repeated except that nylon 12 (Diamide, a product of Dicell Company) was used instead of the polybutylene terephthalate, 2.5% by volume of carbon black having a surface area of 170 m^2/g and an oil absorbance of 2.3 cc/cc was used instead of the activated carbon, and as the lubricant, 7% by volume of silicone oil was used. As Comparative Example 5, only the Diamide was moulded.

EXAMPLE 10.

Example 2 was repeated except that polyacetal copolymer (Duracon M90—02, a product of Polyplastic Co., Ltd.) was used as the base plastic, and as the carrier, 4% by volume of low pressure polyethylene (Hizex Million, a product of Mitsui Petrochemical Industries, Ltd.) having a specific surface area of 1.3 m^2/g and an oil absorbance of 0.7 cc/cc and 15% by volume of Ro 2500 were used. As Comparative Example 6, only M90—02 was moulded in the same way. The results are shown in Table 1.

EXAMPLE 11.

Example 10 was repeated except that turbine oil (special A 180, a product of Maruzen Oil Co., Ltd.) was used instead of the lubricant Ro 2500. The results are shown in Table 1.

TABLE 1

Sample	Tensile Strength	"PV Value of Bearing"	Abrasion resistance
	(Kg/cm²)	(Kg/cm² ×m/min)	(mm)
Comparative Example 1	800	25	Burned
Example 1	510	300	4.2
Example 2	710	400	3.5
Example 3	650	300	3.8
Example 4	650	420	3.5
Example 5	600	300	3.9
Comparative Example 2	786	—	7.5
Example 6	565	—	3.3
Comparative Example 3	1100	—	Burned
Example 7	780	—	3.2
Comparative Example 4	590	—	Burned
Example 8	530	—	6.5
Comparative Example 5	450	—	Burned
Example 9	350	—	3.8
Comparative Example 6	574	55	Burned
Example 10	372	1800	2.9
Example 11	340	1800	3.2

EXAMPLES 12 AND 13 AND COMPARATIVE EXAMPLES 7 AND 8.

Example 10 was repeated except that the amounts of Hizex Million and Ro 2500 were changed as shown in Table 2. The results are shown in Table 2.

TABLE 2

Sample	Amounts "Hizex Million" Polyethylene	"Ro 2500" lubricating oil	Tensile Strength	"PV Value of Bearing"	Abrasion resistance	Injection Mouldability
	(vol.%)	(vol.%)	(Kg/cm^2)	(Kg/cm^2.m/min)	(mm)	-
Comparative Example 7	0.5	1.5	540	60	Burned	Good
Example 12	1	3.0	520	100	8.5	Good
Example 13	12	35.0	230	600	4.8	Good, the oil adhered to the surface of the mould
Comparative Example 8	18	42.0	150	—	5.9	Poor, bad surface condition

It may be seen from the Table 2 that if the amount of the lubricant oil is less than 2%, the abrasion resistance of the moulded article is poor, and if it exceeds 40%, there is a marked reduction in strength, and at the same time, the abrasion resistance is reduced and the mouldability becomes poor.

COMPARATIVE EXAMPLES 9 TO 11.

Example 10 was repeated except that the specific surface area, the oil absorbance, the amount of lubricant to be used, and the ratio of the amount of lubricant to the oil absorbance of the carrier (hereinafter this ratio will be referred to as the "B value") were changed as shown in Table 3.

It may be seen from Table 3 that when the "B value" exceeds 10, the lubricant oil separates during extrusion by means of a biaxial screw, and that if the oil-absorbance is less than 0.2, the strength is remarkably reduced, and the surface condition of the moulded product is poor. The Table also demonstrates the relationship between surface area and oil absorbance.

TABLE 3

	Example 10	Comparative Example 9	Comparative Example 10	Comparative Example 11
Amount of carrier (vol.%)	4	2	12	25
Specific surface area (m^2/g)	1.3	1.3	0.4	0.25
absorbance (cc/cc)	0.7	0.7	0.18	0.10
Amount of lubricant incorporated (vol.%)	15	15	15	15
"B value"	5.35	10.7	6.4	6.0
Tensile strength (Kg/cm^2)	372	—	215	190
Mixing by biaxial extrusion	Good	Oil separates	Good	Good
Mouldability	Good	Oil separates	Good but surface condition poor	Good but surface condition poor

EXAMPLES 14 TO 17.

Kneading and moulding were performed in the same way as in Example 2 using 2.33% by volume of activated carbon having a specific surface area of 1015 m^2/g and an oil absorbance of 5.7 cc/cc, 7% by volume of lubricant Ro 2500, nylon 66 (CM 3001 N) as the base plastic, and at least one antioxidant, 2,2' - methylene*bis* - (6 - *tert.* - butyl - 4-methylphenol) (MPD), 4,4'-butylene*bis*-(6-*tert.*-butyl-3-methylphenol) (BBM) and/or 4,4' - thio*bis* - (6 - *tert.* - butyl - 3 - methylphenol) (WXR), percentages of which are quoted by weight in the following Table 4.

Table 4 shows the improvement in oxidation stability effected by adding an antioxidant.

TABLE 4

Example No.	Antioxidant(s)	Initial Properties · Properties		Tensile Properties After Deterioration*	
		Tensile Strength	Elonation	Tensile Strength	Elongation
		(Kg/cm^2)	(%)	(Kg/cm^2)	(%)
6	None	565	3.5	240	1.5
14	MDP (0.8%)	712	4.2	296	2.0
15	BBM (0.8%)	662	4.0	335	2.2
16	MDP (0.4%) WXR (0.4%)	607	4.1	317	2.4
17	BBM (0.4%) MDP (0.4%)	673	4.4	324	2.2

* The *deterioration* was carried out in a hot air circulating type dryer at 180°C for 4 days. The percentages of the antioxidants quoted are by weight, relative to the whole composition.

EXAMPLE 18.

The procedure of Example 6 was repeated with the additional presence of 10% by volume of Decrolan-4070 (a halogenated alicyclic hydrocarbon-type fire retardant, a product of Hooker Chemical Company) and 0.4% by volume of potassium bichromate and moulded.

EXAMPLE 19.

The same quantities of materials were used as in Example 18. The Decrolan-4070 and the potassium bichromate were pre-mixed with the nylon 66, and extruded by a biaxial screw extruder and then pelletized. The pellets were then mixed with the activated carbon and the lubricant, and the mixture was moulded in the same way as in Example 18.

EXAMPLE 20.

Example 2 was repeated except that 10% by volume of hexabromobenzene and 4% by volume of Sb_2O_3 were further added as a fire retardant.

TABLE 5

Sample	Combustion Test: Burning Time After Igniting for 10 Seconds	Combustion Test: Burning Time After Igniting for 10 Seconds Again	Abrasion resistance (mm)
Comparative Example 2 (nylon 66)	0.3 sec	5 sec	7.5
Example 6	Continued to burn at a rate of 0.68 inch/min		3.3
Example 18	0.7 sec	8 sec	3.8
Example 19	0.9 sec	10 sec	4.0
Comparative Example 1	Continued to burn at a rate of 0.89 inch/min		Burned
Example 2	Continued to burn at a rate of 0.95 inch/min		3.5
Example 20	1 sec	20 sec	4.8

As shown in Table 5, lubricant-containing plastics compositions having markedly improved abrasion resistance and increased fire retardancy can be obtained in accordance with the process of the present invention.

EXAMPLE 21.

Moulding was performed in the same way as in Example 2 using Duracon M90—02 (a polyacetal copolymer, a product of Polyplastic Kabushiki Kaisha), 3% by volume of polyethylene powder having a specific gravity of 1.3 m^2/g and an oil absorbance of 0.7 cc/cc (Hizex Million, a product of Mitsui Petrochemical Industries, Ltd.), 10% by volume of lubricant oil Ro 2500, and 1% by volume of an antistatic agent (Sumistat SP—301 or PP—101, a nonionic surfactant, a product of Sumitomo Chemical Co., Ltd.). The results of the antistatic test determined by means of an honestmeter are shown in Table 6.

TABLE 6

Antistatic Agent	Half Life Period (seconds)	Decay Ratio After 3 Minutes
M90—02 (not containing lubricant)	82	0.25
M90—02 (containing lubricant, but not an antistatic agent)	789	0.73
SP—301	Less than 1	0.05
PP—101	9	0.04

WHAT WE CLAIM IS:—

1. A process of preparing a lubricant-containing synthetic resin composition which comprises (a) mixing a lubricant with at least one carrier; and (b) simultaneously or subsequently mixing the resulting mixture with a synthetic resin; wherein the carrier is an organic or inorganic powder having (i) a melting point higher than the moulding temperature of the synthetic resin, (ii) a specific surface area of at least 0.3 m^2/g and (iii) an oil absorbance as defined herein of at least 0.2 cc of oil per cc of carrier; and the amount of lubricant used is 2 to 40% of the volume of the composition, and not more than 10.00 times the total oil absorbance of the carrier.

2. A process as claimed in Claim 1 wherein a mixer including at least two rotors is used for said mixing.

3. A process as claimed in Claim 1 or 2, wherein the carrier has an oil absorbance of at least 0.6 cc of oil per cc of carrier.

4. A process as claimed in Claim 1, 2 or 3 wherein the carrier has a specific surface area of at least 0.9 m^2/g.

5. A process as claimed in Claim 4 wherein the carrier has a specific surface of at least 3 m^2/g.

6. A process as claimed in any preceding Claim wherein the amount of lubricant used is not more than 5.0 times the oil-absorbance of the carrier.

7. A process as claimed in any of Claims 1 to 6, wherein the powdered carrier is a polyamide, polycarbonate, phenolic resin, epoxy resin or diallyl phthalate resin or poly(tetrafluoroethylene).

8. A process as claimed in any of Claims 1 to 6, wherein the powdered carrier is carbon or an inorganic mineral; or metal, metal oxide, metal nitride or inorganic sulphide.

9. A process as claimed in any preceding claim, wherein the lubricant is a mineral oil or grease, a hydrocarbon, an ester, a polyglycol, a polyphenyl ether, a silicone or a halocarbon compound.

10. A process as claimed in any preceding claim, wherein the lubricant also includes a fatty acid, an aliphatic amide, a metal soap and/or a higher alcohol.

11. A process as claimed in Claim 1, substantially as described herein with reference to the Examples excluding comparative Examples 1 to 8, and to the accompanying drawing.

12. A composition prepared by the process as claimed in any preceding Claim.

13. A composition as claimed in Claim 12 which also contains at least one fire-retardant.

14. A composition as claimed in Claim 12 or 13 which also contains at least one antistatic agent.

15. A composition as claimed in Claims 12, 13 or 14 which also contains at least one antioxidant.

16. A moulded article prepared by moulding a composition as claimed in any of Claims 12 to 15.

GEE & CO.,
Chartered Patent Agents,
Chancery House,
Chancery Lane,
London, WC2A 1QU.
—and—
39, Epsom Road,
Guildford,
Surrey.
Agents for the Applicants.

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1434712 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

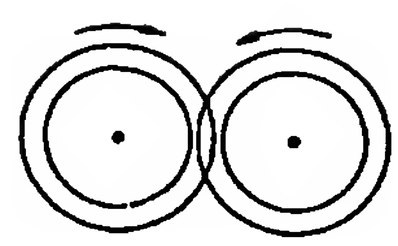

FIG.1

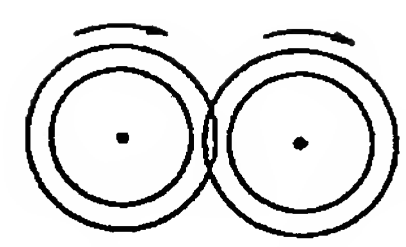

FIG.2

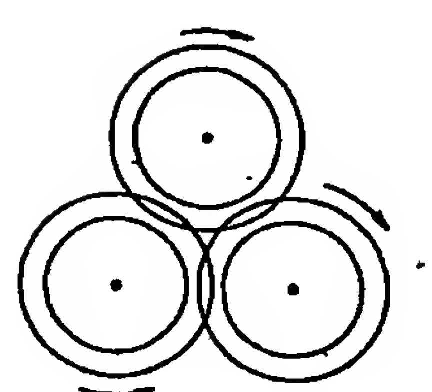

FIG.3

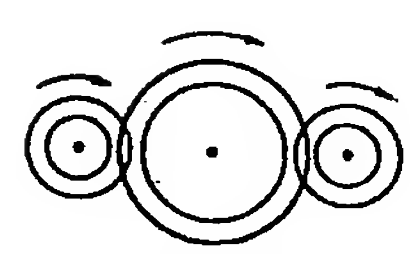

FIG.4